

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 06-316631

(43)Date of publication of application : 15.11.1994

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(51)Int.Cl.

C08G 73/00

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(21)Application number : 04-265529

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(22)Date of filing : 09.09.1992

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### (54) POLYCYCLIC AROMATIC AMINE POLYMER AND ITS PRODUCTION

#### (57)Abstract:

PURPOSE: To obtain a new solvent-soluble polymer, excellent in transparency within a visible region and electric conductivity and capable of manifesting the electric conductivity and a method for producing the polymer.

CONSTITUTION: The polycyclic aromatic amine polymer consists essentially of a polycyclic aromatic amine obtained by subjecting a polycyclic aromatic amine compound to the chemical oxidizing polymerization. Furthermore, the method for producing this polymer is provided.

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#### LEGAL STATUS

[Date of request for examination] 08.09.1999

[Date of sending the examiner's decision of rejection] 30.10.2001

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's  
decision of rejection]

[Date of extinction of right]

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CLAIMS

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[Claim(s)]

[Claim 1] The polycyclic formula aromatic-amine polymer characterized by making into a principal component the polycyclic formula aromatic amine obtained by carrying out the oxidation polymerization of the polycyclic formula aromatic-amine compound chemically.

[Claim 2] The polycyclic formula aromatic-amine polymer according to claim 1 characterized by choosing a polycyclic formula aromatic-amine compound from either of aminonaphthalenes, amino anthracene, or amino quinolines.

[Claim 3] The manufacture method of the polycyclic formula aromatic-amine polymer according to claim 1 characterized by carrying out the oxidation polymerization of the polycyclic formula aromatic-amine compound chemically by the oxidizer.

[Claim 4] The manufacture method of the polycyclic formula aromatic-amine polymer according to claim 3 which an oxidizer is a peroxide and is characterized by carrying out under transition-metal-catalyst coexistence.

[Claim 5] The manufacture method of the polycyclic formula aromatic-amine polymer according to claim 3 or 4 characterized by adding alcohol to a reaction solvent when carrying out the oxidation polymerization of the polycyclic formula aromatic-amine compound chemically.

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[Translation done.]

JAPANESE

[JP,06-316631,A]

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CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE  
INVENTION TECHNICAL PROBLEM MEANS EXAMPLE DESCRIPTION OF DRAWINGS  
DRAWINGS

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## DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the polycyclic formula aromatic-amine polymer which discovers the new conductivity which is the solvent meltable type which makes the main component the polycyclic formula aromatic amine obtained by carrying out the oxidation polymerization of the polycyclic formula aromatic-amine compound, and was excellent in the transparency of a visible region, and its manufacture method.

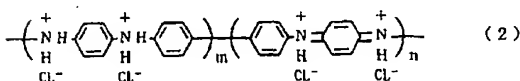
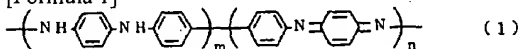
[0002]

[Description of the Prior Art] the polymer obtained by carrying out the polymerization of the five membered ring structure or the ring structure containing hetero atoms, such as a pyrrole, a thiophene, and an aniline, -- as a conductive material -- eye a suitable hatchet -- research is advanced briskly in recent years. Since these polymerization objects can control conductivity free by generally changing the amount of doping, the use to various sensors, a primary cell, a rechargeable battery, an antistatic agent, etc. is examined. Moreover, application of this polymerization object to the conductive layer in the transparent conductivity base material used for the display of a transparent touch switch and liquid crystal display element, electroluminescence, etc. especially recently has come to be considered briskly.

[0003] Generally, polymers, such as a pyrrole, a thiophene, and an aniline, consist of the structure of having pi conjugated system which continues in accordance with a principal chain. However, these compound itself hardly shows conductivity, but it discovers conductivity for the first time by doping. Especially an aniline is the point of electric electric conductivity, and excels other conductive organic materials, for example, polypyrrole, the poly thiophene, etc. in the reversible stability over the repeat of chemical stability and chemical doping, and \*\* doping, and the pan. The reason is presumed because the quinone structure of having a positive charge carrier easily at the time of doping like the \*\* doping state (the following general formula (1)) of an oxidation-type poly aniline and the doping state (the following general formula (2)) by the acid of an oxidation-type poly aniline can be taken.

[0004]

[Formula 1]



Therefore, it is the reason by which the research on the polymerization method of the poly aniline is brought into the limelight, and is considered briskly. It is divided roughly into two, an electrochemical oxidation-polymerization method and a chemical oxidation-polymerization method, as a method of

manufacturing this polymerization object. An electrochemical oxidation-polymerization method is the method of forming a conductive polymerization film using electrochemical reaction, after covering an anionic macromolecule etc. to an electrode top or an electrode, for example, JP,4-139214,A is raised. A chemical oxidation-polymerization method is a method of performing a polymerization under existence of a monomer, an oxidizer, and the acid into an organic solvent or solution, for example, \*\*\*\*\* No. 505892 [ three to ] is raised.

[0005] On the other hand, as an example of manufacture of a polycyclic formula aromatic-amine compound, the example of an electrochemical oxidation polymerization of a naphthylamine is reported. for example, Electrochim.Acta Vol32, pp1223 (1987), J.chem, and Soc.Jpn Vol11, pp2038 (1987), and J.electroanal.Chem. -- JP,2-124938,A is raised with the example of Vol125, pp459 (1981), and diamino naphthalene

[0006] As stated above, there is still no report of the example of a chemical oxidation polymerization using the polycyclic formula aromatic-amine compound (\*\*\*\*\* heterocycle amine compound).

[0007]

[Problem(s) to be Solved by the Invention] Generally, it is hard to dissolve conductive resin in a solvent, and the film formation by the cast method is difficult, and the resin which is easy to dissolve in a solvent has a trouble that conductivity is inferior. Furthermore, a problem that the transparency in a visible region is generally inferior also produces the resin with high conductivity. Moreover, although an electrolytic polymerization method can make a conductive resin base by the comparatively simple method, since a film forming face is limited to an electrode front face, obtaining the film of a large area has a trouble that a manufacturing cost reaches a difficult top highly for an electrolytic oxidation method. Then, the method of manufacturing solvent meltable type conductive resin is examined briskly. For example, the conductive resin (Synth.Metals, Vol18, pp229 (1987)) which introduced the long-chain alkyl group into the 3rd place of a thiophene and a pyrrole is proposed. Or there are also a report if an aniline is oxidized by pyrosulfuric-acid ammonium, that the meltable type poly aniline (Polym.Prepr., Vol38, pp638 (1989)) will be obtained, and a report if a methoxy machine is introduced into the ortho position of an aniline, that a meltable type poly aniline (Synth.Metals, Vol25, pp235 (1988)) will be obtained. Simply, though regrettable, transparency does not go satisfactorily. On the other hand, there is also a report that transparent conductive resin (Bull.Amer.Phys.Soc., Vol30, pp607 (1985)) is obtained in the state of a dope in a visible region by carrying out electrolytic polymerization of the iso thianaphthene.

[0008] As explained above, there is still no development report of the conductive resin which is a solvent meltable type and was excellent in transparency in the visible region.

[0009]

[Means for Solving the Problem] This invention persons found out that this purpose could be attained by carrying out the oxidation polymerization of the polycyclic formula aromatic-amine compound chemically, as a result of examining wholeheartedly the field excellent in the chemical stability and the reversible stability of a polymerization object aiming at development of the conductive resin which is the energize purpose and was excellent in meltable, high conductivity, and the transparency in a visible region at the solvent paying attention to the aromatic-amine compound.

[0010] That is, this invention relates to the polycyclic formula aromatic-amine polymer which discovers the new conductivity which was excellent in meltable, high conductivity, and the transparency in a visible region at the solvent, and its manufacture method by easy operation of carrying out the oxidation polymerization of the polycyclic formula aromatic-amine compound chemically.

[0011] this invention is explained further below at a detail.

[0012] The polycyclic formula aromatic-amine polymer in this invention makes a principal component the polycyclic formula aromatic amine obtained by carrying out the oxidation polymerization of the polycyclic formula aromatic-amine compound chemically.

[0013] As a polycyclic formula aromatic-amine compound used by this invention, amino quinolines, such as amino anthracene, such as aminonaphthalenes, such as 1-aminonaphthalene and 2-aminonaphthalene, a 1-amino anthracene, a 2-amino anthracene, and a 5-amino anthracene, a 2-amino

quinoline, a 3-amino quinoline, a 1-amino isoquinoline, and a 3-amino isoquinoline, an aminoacridine, an amino cinchona bark lysine, etc. are raised, for example. Of course, you may use the compound which introduced the alkoxy group of carbon numbers 1-20 into the ring in order to raise the solubility of a generation resin further.

[0014] The polycyclic formula aromatic-amine polymer in this invention can be easily manufactured by adding an oxidizer after dissolving carrying out the oxidation polymerization of the polycyclic formula aromatic-amine compound chemically by the oxidizer, i.e., an above-mentioned polycyclic formula aromatic-amine compound, in a reaction solvent. Furthermore, in order to advance polymerization reaction smoothly, it is desirable to add a proton acid.

[0015] Although it does not restrict especially as a reaction solvent used here, it is desirable for that in which the above-mentioned amine compound (monomer) is dissolved to use an acid water-soluble solvent desirable especially, and in order to dissolve the target monomer, a proton acid, and an oxidizer further, the mixture of water and an organic solvent is good. Although the organic solvent at this time is not limited especially if it is an organic solvent which does not settle each above-mentioned compound, ether, such as nitril, such as an acetonitrile and a benzonitrile, a tetrahydro furan, a dioxane, and dibutyl ether, N-methyl pyrrolidone, a dimethyl sulfoxide, a water-soluble weak acid like an acetic acid, etc. are raised, for example. Although especially the mixing ratio of water and an organic solvent is not limited, the standard of the organic solvent added in water has the desirable grade which a monomer, a product, and other additives dissolve.

[0016] Furthermore, it is good to add alcohols, such as alcohol, for example, a methanol, ethanol, and ISO (or n) propanol, for obtaining the polymer of high transparency, without reducing conductivity. Although especially the addition of alcohols is not limited, its addition of 5 volume [ of an overall-reaction solvent ] % to 30 volume % is the most desirable.

[0017] Especially with [ an acid dissociation constant  $pK_a$  ] 3.5 [ or less ], it does not limit as a proton acid used by this invention. For example, organic acids, such as inorganic acids, such as a hydrochloric acid, a sulfuric acid, a nitric acid, perchloric acid, and a hydrofluoric acid, a BENSEN sulfonic acid, a toluenesulfonic acid, a methanesulfonic acid, an ethane sulfonic acid, a polystyrene sulfonic acid, a chondroitin sulfuric acid, and a trifluoroacetic acid, are raised. Although it is dependent on the kind of oxidizer used as an addition of these acids, generally it is good to use within the limits of the two to 4 time equivalent preferably more than the double-precision equivalent of an oxidizer.

[0018] The oxidizer used by this invention is more desirable at the soluble point to the solvent of the resin which using a hydrogen peroxide generated and the point that a price is cheap, and the point that still a lot of metallic compounds in a rough generation polymerization object are not contained, although manganese dioxide generally used, a hydrogen peroxide, a sodium persulfate, potassium persulfate, pyrosulfuric-acid ammonium, a potassium dichromate, a sodium dichromate, perchloric acid iron, a ferric chloride, etc. are raised. The addition of an oxidizer is 1-1.3 mols preferably that what is necessary is just one mols or more of a monomer.

[0019] When an oxidizer is a hydrogen peroxide in this invention, it is necessary to add a transition metal catalyst to a reaction solvent. As such a transition metal catalyst, metals or these compounds, such as iron, copper, chromium, cobalt, and nickel, are desirable, and what shows catalase activity and Fenton's-reagent activity like an iron (II) compound, an iron (III) compound, and a copper (II) compound especially is desirable. a transition metal catalyst -- usually -- 0.5-mol % to five-mol% of an oxidizer -- it is added

[0020] An example which manufactures a polymer according to the chemical oxidation polymerization using the monomer in this invention is described below.

[0021] First, alcohol will be added, if a monomer is agitated with sufficient specified quantity \*\*\*\* after mixing an organic solvent if needed [ water and if needed ] for the specified quantity, next there is need. What is necessary is just to add alcohol to obtain the polymer which discovers the conductivity which was more excellent in transparency, as \*\*\*\* explained. Then, after putting in a proton acid and agitating well, the said weight grade addition of the organic solvent is again carried out with the first stage if needed. The reason for dividing and putting in an organic solvent here is for obtaining a conductive

higher resin. Of course, when the resin of conductivity high only at once the first stage is obtained depending on the monomer to be used, it is not necessary to divide and put in. Next, it adds in transition metals, an oxidizer, and this order, and a polymerization is performed at predetermined temperature. Although what is necessary is for the range of the polymerization temperature at this time just to be 100 degrees C - -80 degrees C, the range of 40 degrees C - 0 degree C deals with it, and it is the most desirable a top. Since polymerization reaction is stopped, reaction mixture can be obtained by iced water, succeedingly, it can wash by the organic solvent and a polymer can be obtained by washing and making it dry at the end.

[0022] High conductivity can be made to discover in this invention by doping, while oxidizing according to chemistry oxidization or electrolytic oxidation if needed, after carrying out direct \*\* doping of the polymer manufactured according to the above-mentioned oxidation polymerization, without [ chemical reduction and ] returned or returning electrochemically. As a reducing agent used for chemical reduction, hydrogenation metals, such as hydrazines, such as a hydrazine, hydrazine hydrate, and a phenylhydrazine, lithium-hydride aluminum, and a sodium borohydride, etc. can be raised. Usually, although 1-10 mols per 1 nitrogen atom of a polymer of chemistry reducing agents are used, they are not necessarily limited to this.

[0023] What is necessary is just to neutralize the proton acid as a dopant in an alkali, in order to perform \*\* doping. Although such an alkali especially is not limited, metal hydroxides, such as aqueous ammonia, a sodium hydroxide, a potassium hydroxide, and a lithium hydroxide, are used preferably. Any compound can be used, if it has sufficient oxidizing power to oxidize this polymer as an oxidizer used here and has electronic receptiveness. For example, salts, such as Lewis acids, such as halogens, such as chlorine, a bromine, an iodine, and a fluorine, a 5 fluoride arsenic, 5 antimony fluoride, 3 fluoride boron, a boron trichloride, a ferric chloride, a stannic chloride, a titanium tetrachloride, a zinc chloride, and a cupric chloride, a sodium perchlorate, and a potassium perchlorate, etc. are raised.

[0024] Moreover, as an acid for making it dope, organic sulfonic acids, such as strong acid, such as a hydrochloric acid and a sulfuric acid, a methanesulfonic acid, an ethane sulfonic acid, a benzenesulfonic acid, and a toluenesulfonic acid, are raised. Moreover, macromolecule proton acids, such as a polystyrene sulfonic acid, a polyvinyl sulfonic acid, and the poly allyl-compound sulfonic acid, can also be used.

[0025] The process of a conductive film is described as an example below.

[0026] First, the polymer of this invention is dissolved in a solvent. Especially if the solvent used at this time is a solvent in which it is easy to dissolve a polymer, it will not be limited. For example, acid solution, such as alkaline-water solutions, such as polar solvents, such as DMF, DMSO, and NMP, ammonia, and caustic alkali of sodium, formic acid, a hydrochloric acid, and a sulfuric acid, etc. is raised. Since solubility is increased at this time, addition may be added to a solvent, and in order to raise an application property, you may add salts, such as chlorination lithium, for a surfactant etc. further. Then, it applies to a substrate. As the method of application, a spin application or which methods, such as the roll-coater method, print processes, and the cast method, may be used. After an application, a solvent is flown and a film is dried. Then, the obtained film is doped by the method immersed into an acidic solution, or the method of making acids, such as a hydrochloric acid, contact by the gaseous phase, and conductivity is raised. Moreover, when this polymer is obtained as a reductant containing many leuco EMERARU DIN type polymer analogous-NH-machines in the poly aniline, by making it react with the above-mentioned oxidizer before film formation or after film formation, the principal chain structure from which conjugated system developed is made to be able to form, and doping can raise conductivity further.

[0027] In addition, conductivity is discovered, even if it dopes by the same method as the above as the method of evaluation, after compressing a polymer (it compresses by the pressure of 500 kg/cm<sup>2</sup>). However, generally the conductivity in this case is inferior compared with the case where it is made a film as mentioned above.

[0028]

[Example] Hereafter, although an example explains this invention in more detail, this invention is not



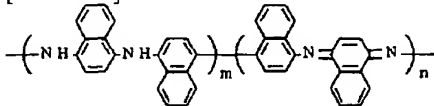
limited to these.

[0029] Succeedingly, 2.9ml of concentrated sulfuric acids, after putting refined 1-aminonaphthalene 0.54gr into the 200ml flask with a three-way cock with example 1 stirring equipment acetonitrile 15ml and 60ml of water and stirring well, temperature was controlled at 30 degrees C in the thermostat, again, 15ml and FeSO<sub>4</sub>·7H<sub>2</sub>O were added to 20mg, 0.5ml (31% article) of hydrogen peroxide solution was added for the acetonitrile to this order, and the reaction was performed for 40 hours. Next, the polymer was settled in iced water for the purpose of a reaction halt and impurity removal, it carried out the \*\* exception, the polymer was carried out the after [ 3 - 4 hour stirring washing ] \*\* exception in aqueous ammonia in the methanol the back according to 3 - 4-hour stirring washing, and \*\*, operation with washing was succeedingly performed in the methanol again, and the polymer was refined. Then, the vacuum drying was performed and the polymer was obtained. Yield was 85%.

[0030] When GPC measurement was performed to DMF by making into an eluate the solution which carried out 10mmol dissolution of the lithium bromide, the molecular weight of this obtained polymer was 4.3x10<sup>3</sup> gr/mol (polystyrene reduced property) and degree of dispersion (Mw/Mn) 1.42 in weight average molecular weight. When <sup>13</sup>CNMR(s) of this polymer were measured, as shown in [drawing 1](#), the peak originating in C1 and C4 of a monomer disappeared, and absorption of a deformation vibration outside a field strong against 760cm<sup>-1</sup> was seen by the infrared absorption spectrum of [drawing 2](#). Moreover, in <sup>1</sup>HNMR shown in [drawing 3](#), the integration ratio of the proton in a ring and the proton of NH was 17:1. This shows that this polymer has taken the structure of a lower formula.

[0031]

[Formula 2]



After dissolving this polymer in a NMP solvent so that it may become 7.0x10<sup>-5</sup> mol/l. concentration, when the extinction property was measured using 1cm cell, as shown in [drawing 4](#), the absorption maximum was in 295nm, and the absorbancy index epsilon was 7140mol<sup>-1</sup>cm<sup>-1</sup> in the DMF solvent. Moreover, he can understand that there is no absorption peak within the limits of 400nm - 700nm from [drawing 4](#), and this polymer is excellent in transparency in a visible region since absorption is small. Furthermore, when the solubility of this polymer was investigated, it turns out that it melts in polar organic solvents, such as DMF, DMSO, and NMP, and a sulfuric acid, and formic acid well, and dissolves in chloroform and THF a little. Moreover, after applying the pressure of 500 kg/cm<sup>2</sup> to this polymer using the molding machine for infrared spectrums, making the molding object and being immersed into 35% solution of hydrochloric acid for 12 hours, when the electrical conductivity of this molding object was measured, the value of 3.8x10<sup>-4</sup> S/cm was shown. Moreover, the electrical conductivity in the case of the molding object exposed to the atmosphere of iodine for 12 hours showed 2.4x10<sup>-3</sup> S/cm and good electrical conductivity.

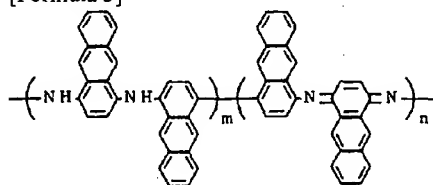
[0032] 1-aminonaphthalene 0.54gr refined acetonitrile 15ml and 76ml of water in the 200ml flask with a three-way cock with example 2 stirring equipment -- putting in -- succeedingly -- methanol 15ml -- further, 2.9ml of concentrated sulfuric acids, temperature was controlled at 30 degrees C in the thermostat by stirring with the sufficient addition back, again, 15ml and FeSO<sub>4</sub>·7H<sub>2</sub>O were added to 20mg, 0.5ml (31% article) of hydrogen peroxide solution was added for the acetonitrile to this order, and the reaction was performed Next, iced water, a methanol, aqueous ammonia, and the methanol performed the same refining as an example 1 for the purpose of a reaction halt and impurity removal, the vacuum drying was performed, and the polymer was obtained. Yield was 82%. The electrical conductivity after measurement of the extinction of a visible region and iodine doping was measured on the same conditions as an example 1. Consequently, it turns out that the transparency in a visible region is excellent from the extinction property of [drawing 5](#). The result with as good electrical conductivity as 2.6x10<sup>-3</sup> S/cm was obtained.

[0033] Further, after putting refined 1-amino anthracene 0.27gr into the 300ml flask with a three-way cock with example 3 stirring equipment acetonitrile 80ml and 80ml of water and stirring well, temperature was controlled at 30 degrees C in the thermostat, 0.68ml of concentrated sulfuric acids and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  were added to 10mg, 0.22ml (31% article) of hydrogen peroxide solution was added to this order, and the reaction was performed for 22 hours. Next, the same refining as iced water, a methanol, aqueous ammonia, a methanol, and an example 1 was performed for the purpose of a reaction halt and impurity removal, the vacuum drying was performed, and the polymer was obtained. Yield was 92.5%.

[0034] When the determination of molecular weight was performed on the same measurement conditions as an example 1, the molecular weight of this obtained polymer was  $5.6 \times 10^3$  gr/mol (polystyrene reduced property) and degree of dispersion ( $M_w/M_n$ ) 1.23 in weight average molecular weight. When  $^{13}\text{C}$ NMR(s) of this polymer were measured, as shown in [drawing 6](#), the peak originating in C1 and C4 of a monomer disappeared, and in  $^1\text{H}$ NMR, the integration ratio of the proton in a ring the proton of NH was 16:1 (90MHz). This is presumed that this polymer has taken the structure of the following formula.

[0035]

[Formula 3]



Although the reduction in a weight began from near 250 degree C when the pyrolysis character under the nitrogen-gas-atmosphere mind of this polymer was measured with the pointing thermal-analysis machine (10-degree-C programming rate for /), even if it carried out the temperature up to 900 degrees C, it turns out that the property the polymer of at most 22% and this invention excelled [ property ] in weight reduction also to thermal resistance is shown.

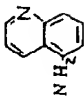
[0036] Although the absorption maximum will be looked at by 290nm, 300nm, 330nm, and 350nm as shown in [drawing 7](#) if the extinction property of a visible region is measured by the same method as an example 1 after dissolving this polymer in a NMP solvent so that it may become the concentration of  $5.8 \times 10^{-5}$  mol/l, he can understand that there is no absorption peak within the limits of 400nm - 700nm, and this polymer is excellent in transparency in a visible region since absorption is small. Furthermore, when the solubility of this polymer was investigated, it turns out that it melts in a polar organic solvent and formic acid, such as DMF, DMSO, and NMP, well, and dissolves in chloroform and THF a little.

[0037] After performing a polymerization on the conditions which control temperature at 30 degrees C in a thermostat, and are shown in Table 1 after putting refined 5-amino quinoline 0.72gr into a 100ml flask with a three-way cock an example 4 - with 6 stirring equipment 50ml of water and stirring well, the polymer was settled in iced water, the polymer was performed after washing, the vacuum drying was performed in several hour methanol, and the polymer (a) was obtained. The low sake, in the filtrate carried out the \*\* exception out of iced water, reaction yield added hydrogen peroxide solution again, and obtained the polymer (b) after one-day neglect using the same washing / dryness method.

[0038]

[Table 1]

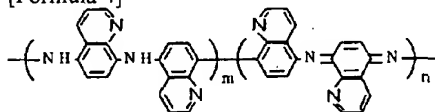
実施例	キノリン*1 g r	溶媒(水) ml	硫酸 mmol	硫酸鉄*2 mgr	過酸化水素*3 mmol	重合時間 hr	収率 %	分子量 g/mol
4 a法 b法	0.72	100	8	20	3.15 3.15	25 24	14 14	$4.5 \times 10^3$
5 a法 b法	0.72	400	5	40	1.60 1.60	25 24	6 34	$4.5 \times 10^3$
6 a法 b法	0.72	100	5	80	6.00 6.00	25 24	40 0	$4.0 \times 10^3$

\*1:キノリンとは  \*2:  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  \*3: 31%濃度の水溶液品

That to which this polymer is also carrying out structure of the following formula from  $^{13}\text{C}$ NMR(s) and  $^1\text{H}$ NMR is presumed.

[0039]

[Formula 4]



Although the absorption maximum will be looked at by 285nm as shown in drawing 8 if the extinction property of a visible region is measured by the same method as an example 1 after dissolving this polymer in a DMF solvent so that it may become the concentration of  $9.1 \times 10^{-5}$  mol/l, there is no absorption peak within the limits of 400nm - 700nm, and since absorption is small, it turns out that this polymer is excellent in transparency in a visible region. Furthermore, when the solubility of this polymer was investigated, it turns out that it melts in polar organic solvents, such as DMSO and NMP, and formic acid, a hydrochloric acid, a sulfuric acid, aqueous ammonia, and caustic-alkali-of-sodium solution well, and dissolves in DMF a little.

[0040] After putting refined 5-amino isoquinoline 0.6gr into the 200ml flask with a three-way cock an example 7 - with 9 stirring equipment acetonitrile 10ml and 100ml of water and stirring well, temperature was controlled at 30 degrees C in the thermostat, and the polymerization was performed on the conditions shown in Table 2. Next, it was made to precipitate in iced water for the purpose of a reaction halt and impurity removal, and washing was performed in the methanol for several hours, the acetone was made to reprecipitate after remelting to aqueous ammonia at a degree, the vacuum drying was performed, and the polymer was obtained.

[0041]

[Table 2]

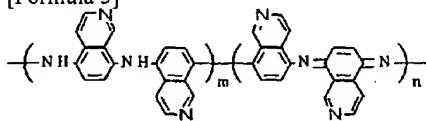
実施例	キノリン*1 gr	溶媒 ml	硫酸 mmol	硫酸鉄*2 mgr	過酸化水素*3 mmol	重合時間 hr	収率 %	分子量 g/mol
7	0.60	H <sub>2</sub> O 100 CH <sub>3</sub> CN 10	4	80	5.4	18	16	$3.4 \times 10^3$
8	0.60	H <sub>2</sub> O 100 CH <sub>3</sub> CN 10	12	80	5.4	24	12	$3.3 \times 10^3$
9	0.60	H <sub>2</sub> O 27.5	4	10	5.0	24	25	$6.7 \times 10^3$

\*1;キノリンとは  \*2: FeSO<sub>4</sub> · 7H<sub>2</sub>O \*3: 31%濃度の水溶液品

That to which this polymer is also carrying out structure of the following formula from <sup>13</sup>CNMR(s) and <sup>1</sup>HNMR is presumed.

[0042]

[Formula 5]



When the solubility of this polymer was investigated, it turns out that it melts in polar organic solvents, such as DMF, DMSO, and NMP, and formic acid, aqueous ammonia, and caustic-alkali-of-sodium

solution well, and dissolves in a methanol, ethanol, THF, a sulfuric acid, and a hydrochloric acid a little. Moreover, when DMF was made to carry out the lithium-bromide 10 mmol/l dissolution, it turns out that the polymer of this invention increases solubility further.

[0043]

[Effect of the Invention] As explained above, since it is a solvent meltable type, and it excels in the transparency in a visible region and doping and \*\* doping have further the structure which can be performed stably and in reversible, the polymer by this invention is suitable for material, such as a conductive layer in various sensors, a primary cell, a rechargeable battery, and a transparent conductivity base. furthermore, the thing for which the polymer of this invention manufactures the polymer which discovers conductivity by the easy operation of a chemical oxidation polymerization -- eye a possible hatchet -- it can manufacture cheaply and industrial value is also large

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[Translation done.]

\* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] Drawing having shown <sup>13</sup>CNMR chart of 1-aminonaphthalene (monomer) and this polymer.

[Drawing 2] Drawing having shown the infrared absorption spectrum of the polymer of 1-aminonaphthalene.

[Drawing 3] Drawing having shown <sup>1</sup>HNMR chart of the polymer of 1-aminonaphthalene.

[Drawing 4] the spectrum of the polymer of 1-aminonaphthalene -- drawing having shown the chart

[Drawing 5] the spectrum of the polymer of 1-aminonaphthalene when adding alcohol to a reaction solvent -- drawing having shown the chart

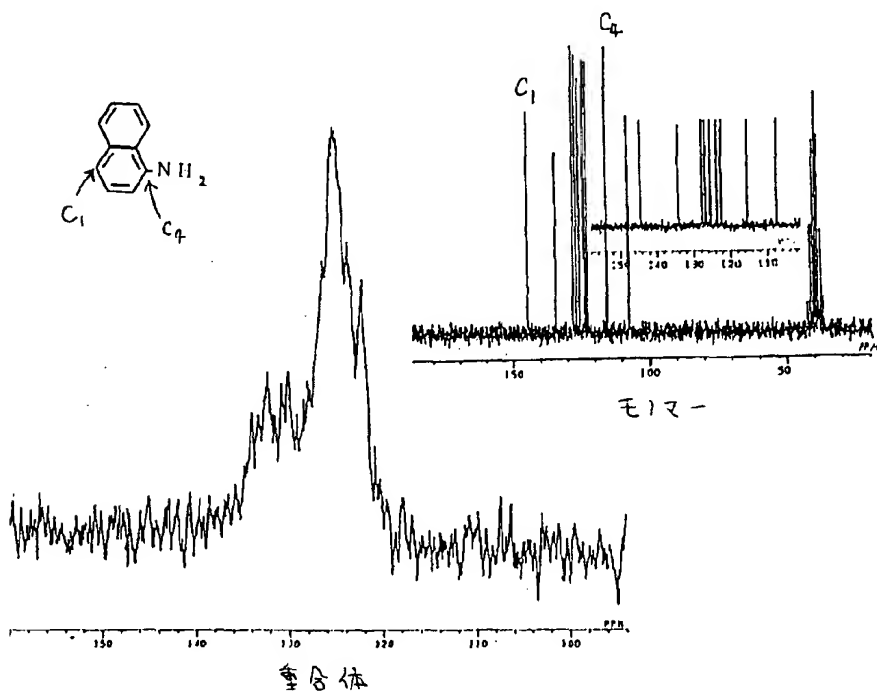
[Drawing 6] Drawing having shown <sup>13</sup>CNMR chart of a 1-amino anthracene (monomer) and this polymer.

[Drawing 7] the spectrum of the polymer of a 1-amino anthracene -- drawing having shown the chart

[Drawing 8] the spectrum of the polymer of a 5-amino quinoline -- drawing having shown the chart

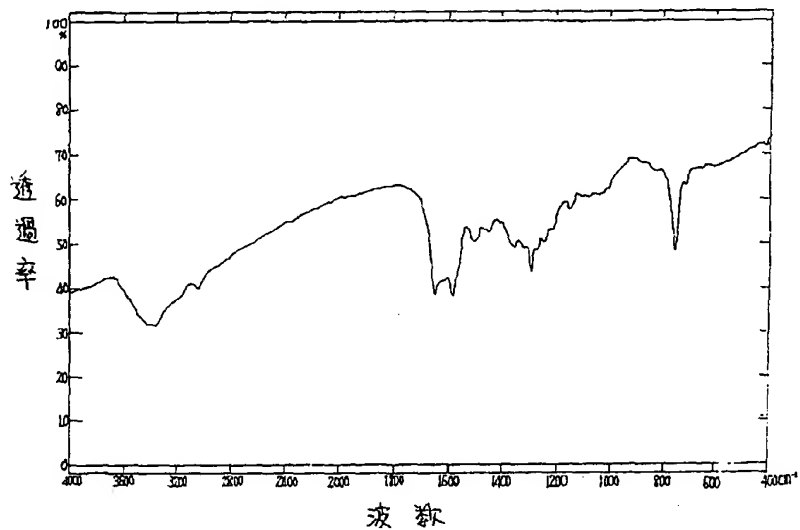
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[Translation done.]

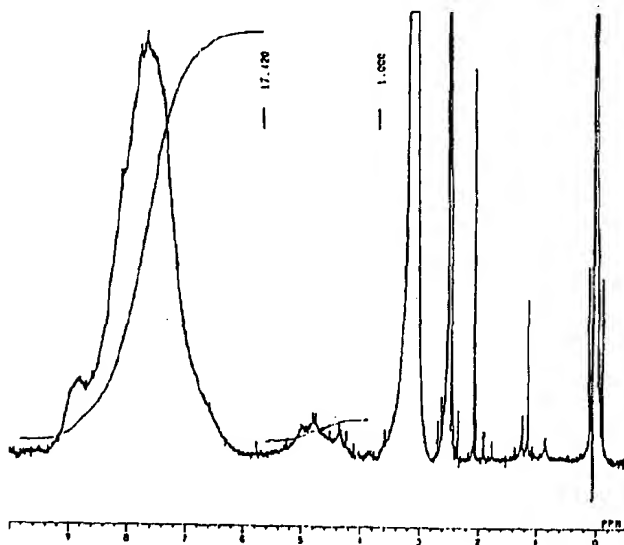
Drawing selection drawing 1

[Translation done.]

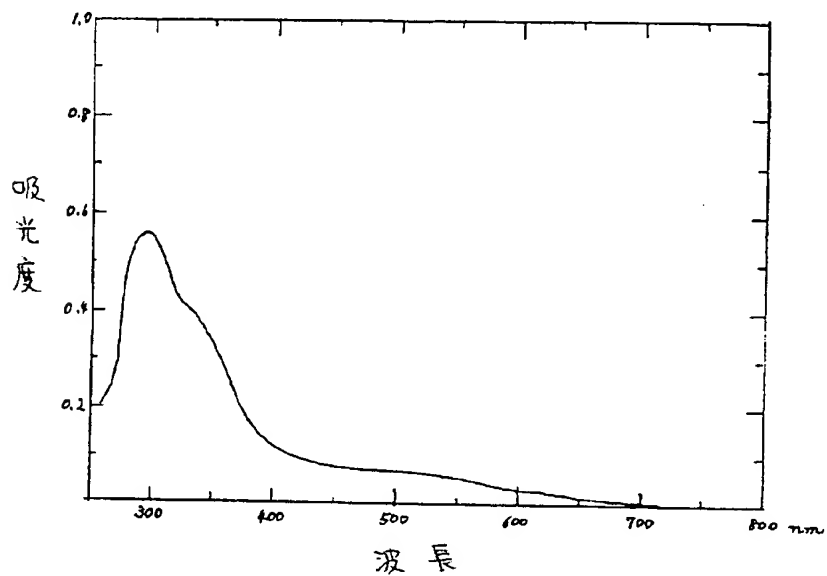


Drawing selection drawing 2 ▾

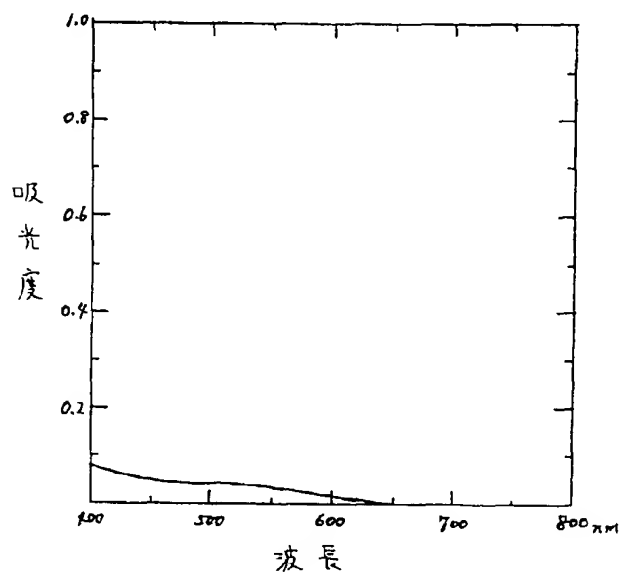
[Translation done.]

Drawing selection drawing 3

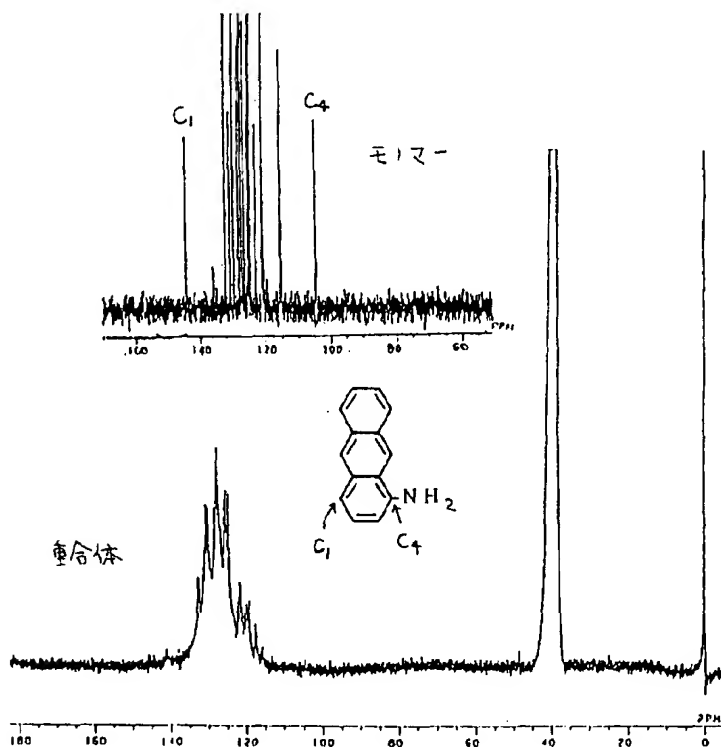
[Translation done.]

Drawing selection drawing 4 ▾

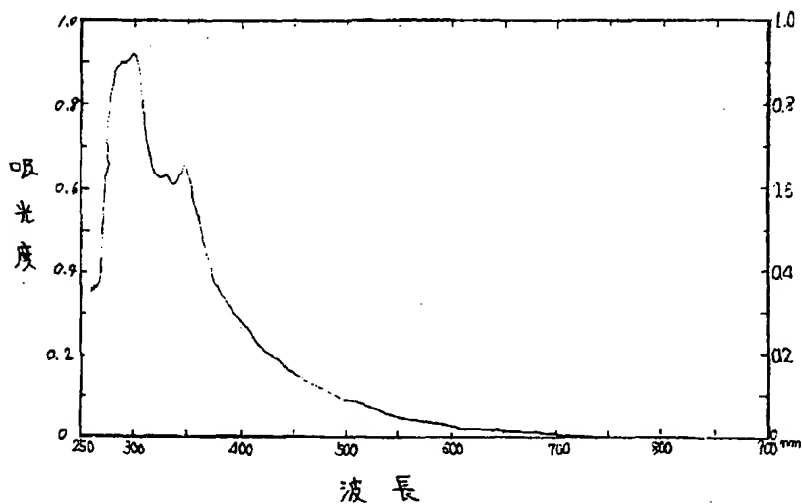
[Translation done.]

Drawing selection drawing 5 ▾

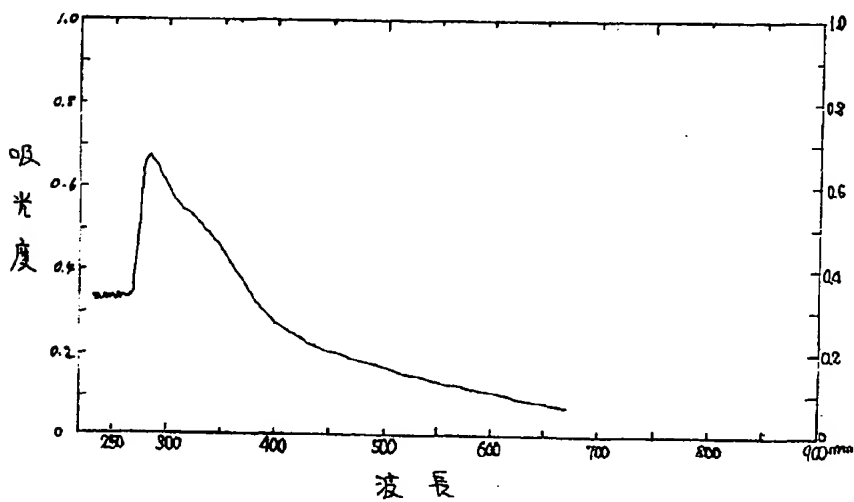
[Translation done.]

Drawing selection drawing 6

[Translation done.]

Drawing selection drawing 7 ▾

[Translation done.]

Drawing selection drawing 8 ▾

[Translation done.]